(12) **UK Patent Application** (19) **GB** (11) **2 059 574** **A**

(54) **Absorption cell gas monitor**

(57) An absorption cell gas monitor for measuring and monitoring the concentration of a specific gas, such as ozone, in an ambient atmosphere comprises first and second absorption cells (30) and (34) through each of which is passed alternately an ambient sample from an inlet port (12) and containing the specific gas to be monitored and an ambient sample from which the specific gas has been removed by a chamber (14) connected to the inlet port (12), each cell receiving the sample from the inlet port (12) while the other cell receives the sample from the chamber (14). Radiation from a source (60) having a wavelength absorbed by the specific gas is directed through each cell (30), (34) and the intensity of the radiation transmitted by each cell is detected by a detector (66), (68) respectively, the intensities being compared and computed in a stepped sequence in a microcomputer (72) to provide output data on the concentration of the specific gas in the ambient sample.

The drawing originally filed was informal and the print here reproduced is taken from a later filed formal copy.
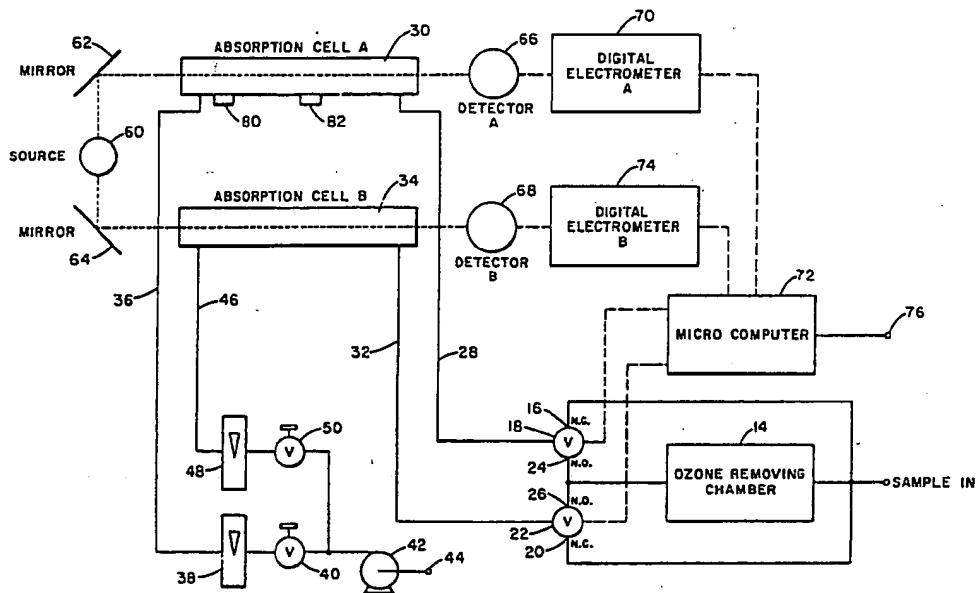

FIG. 1

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SPECIFICATION
Absorption cell gas monitor

This invention relates to absorption cell gas monitors for monitoring the concentration of a specific gas or vapour in an ambient atmosphere, and is particularly concerned with the rapid cancellation in real time of first order errors caused by absorption of radiation by gases and/or vapours other than that being monitored and by variations in output intensity of the source of radiation, as well as second order errors caused by optical asymmetry and reflectivity changes.

The presence or concentration of a gas or vapour in a sample is frequently determined by its characteristic absorption or attenuation of radiation of a particular wavelength. For any given gas or vapour to be measured or monitored, the sample is irradiated by energy of a wavelength which is significantly absorbed by the gas or vapour being monitored, but not by other gases or vapours which are expected to be present in the sample, and the transmission loss suffered by the radiation is determined.

The range of wavelengths which may be used in absorption cell gas monitors is rather wide. For example, gases such as ozone and sulphur dioxide, and vapours such as acetone and benzene significantly absorb radiation of wavelengths in the untraviolet region, whereas wavelengths in the infrared region are readily absorbed by gases such as NO_2, CO_2 and H_2S, and by water vapour.

The present invention is primarily concerned with ozone monitoring, but is also applicable to absorption cell gas monitors for other gases and vapours, provided appropriate selection of the radiation source and other components of the monitor is made.

In a basic arrangement for monitoring the presence or concentration of ozone or any other specific gas in a sample, a comparison is made between the transmission of radiation of a suitable wavelength through an absorption cell containing a sample from which the specific gas has been removed and the transmission of similar radiation through the cell when it contains a sample from which none of the specific gas has been removed. The theoretical basis for such arrangements is found in the Beer-Lambert Law:

$$I/I_0 = e^{(-kLc)}$$
where

I   = the intensity of radiation transmitted by a sample containing the specific gas;

I_0 = the intensity of radiation transmitted by a sample having the specific gas removed;

k   = the absorption coefficient of the specific gas at the wavelength of the radiation;

c   = the concentration of the specific gas in the sample;

L   = the length of the absorption cell;

and,

e   = the natural logarithmic base.

Generally, in known absorption cell gas monitors, I_0 is measured first, using a suitable photoelectric device, and then I is measured to determine the difference in transmission through the absorption cell, and the concentration of the specific gas in the sample is simply calculated using the above Beer-Lambert equation.

Because it is difficult to maintain a constant output from the source of radiation, which is usually a light source, it has been common to place a reference photoelectric detector in a position to view directly the light source, and the output of the reference detector is used to compensate for fluctuations in the output of the source.

Measurements made in the manner described have produced some useful results, but the accuracy of those results suffers for several reasons. For example, the sample may be passed through a suitable chamber containing a scrubber or other means for removing the specific gas, but other gaseous and vaporous components which absorb radiation at the particular wavelength may remain. If the concentration of such other components varies with time, a measurement of I_0 made prior to that of I may no longer be valid when I is measured.

Also, in procedures in which a single absorption cell is used, in addition to the possible errors resulting from the time delay between the measurement of I_0 and the measurement of I, data-gathering time is lost because it is necessary to purge or flush the cell with the sample from which the specific gas has been removed to establish a "zero" base before the measurements are made. Typically, one might

254 nm. The light is trained upon a first mirror 62 and a second mirror 64. From the mirror 62, light is reflected through the length of the absorption cell 30 to a detector 66. The detector 66 may be any of several known devices such as a solar-blind vaccum photodiode detector sensitive to 254 nm radiation. The output current of the detector 66 is determined by the intensity of radiation of the preselected wavelength impinging upon the detector. In this fashion, an efficient monochromator for the detection   5
of ozone is formed. At the same time, light from the source 60 is reflected by the mirror 64 through the length of the absorption cell 34 to a detector 68 which may be similar in all respects to the detector 66, a second monochromator being thus formed.

In addition to the solid lines indicating gas flow and dotted lines indicating light paths, dashed
10   lines show the path of electrical signals. A signal in the form of current is derived from the detector 66   10
and is coupled to a reference digital electrometer 70 from which it is passed to a microcomputer unit 72 which may generally correspond to the comparable unit disclosed in the cited parent application Serial No. 051,651. That unit, as noted, includes a standard 8-bit microprocessor and other elements described below. At the same time as the signal is derived from the detector 66, a signal is also
15   generated in the detector 68, coupled to a digital electrometer 74 and also passed to the unit 72.   15
Besides providing data for display or other use at an output terminal 76, the microprocessor of element 72 is programmed to provide a suitable output to control the operation of the solenoid valves 18 and 22 as described below.

The signals derived from the detectors 66 and 68 may be processed by first being converted to
20   voltages and then to frequencies by voltage-to-frequency converters. The output of the converters may   20
then by counted by counters for a specific length of time determined by the microprocessor 72 and integrated in the manner described below.

In operation, a cycle of the ozone monitor begins as the solenoid valve 18 is switched to route the sample from the ozone-removing chamber 14 into the cell 30 (absorption cell A). At the same time, the
25   solenoid valve 22 is switched so as to route the sample directly from the port 12 into the cell 34   25
(absorption cell B). After an appropriate flush time, typically 4—5 seconds, I_0 for the cell 30 is determined, and I for the cell 34 is detemined.

The intensities of the currents from the detectors 66 and 68 may be integrated over a period of one second, and these values are stored in the memory of the microcomputer 72. These values for the
30   first integration period may conveniently be denoted $I_0(A,t=1)$ and $I(B,t=1)$ for the first half of a cycle.   30

At the end of the first integration period, a signal from the microcomputer 72 triggers the solenoid valves 18 and 22 so that sample passes directly from input 12 through the solenoid 18 to the cell 30 and simultaneously the ozone-free output of the chamber 14 passes through the solenoid 22 to the cell 34. After a flush of about 4—5 seconds, the intensities of the currents from the detectors are integrated
35   once more over a period of one second. During this second half of the cycle, the values measured for   35
this second integration period may be denoted $I(A,t=2)$ and $I_0(B,t=2)$.

The Beer-Lambert equations for times t=1 and t=2 are:

$$\frac{I(B,t=1)}{I_0(B,t=1)} = e^{-kL(B)c(t=1)}$$

                                                         (1)

$$\frac{I(A,t=2)}{I_0(A,t=2)} = e^{-kL(A)c(t=2)}$$ (2)

40   where L(A), L(B) are the lengths of absorption cells A and B, c(t=1) and c(t=2) are the ozone   40
concentrations at times t=1 and t=2, $I_0(B,t=1)$ is the photocurrent that would have been measured by detector B during the time t=1 if the sample flowing during time 1 had its ozone removed, and $I_0(A,t=2)$ is similarly defined photocurrent for detector A at time t=2.

As is clear from their definition, the values $I_0(B,t=1)$ and $I_0(A,t=2)$ cannot be measured directly. If
45   the stability of the lamp system in the detectors from time t=1 to time t=2 were sufficient, we could   45
simply set $I_0(B,t=1)$, $I_0(A,t=2)$ equal to the measured values $I_0(B,t=2)$ $I_0(A,t=1)$. In practice, sufficient stability cannot be obtained, primarily because of variation of the lamp intensity with time (stabilities of one part in 10^5 are needed for detection of ozone concentration of one part per billion). Thus, the simple assumptions $I_0(A,t=2) = I_0(A,t=1)$, $I_0(B,t=1) = I_0(B,t=2)$ cannot be used. Let d(A) and d(B) be the
50   factors expressing the change in lamp intensity between time t= and time t=2, as measured by   50
detectors A and B, respectively. We will have:

$$I = (A,t=2) = d(A) I_0(A,t=1) \text{ and } I_0(B,t=2) = d(B)I_0(B,t=1),$$ (3)

$$\frac{I(A,t=2)\ e^{+k_i}\ c_i(t=2)L}{I_0(A,t=1)\ e^{+k_i}\ c_i(t=1)L} \cdot \frac{I(B,t=1)\ e^{+k_i}\ c_i(t=1)L}{I_0(B,t=2)\ e^{+k_i}\ c_i(t=)L} = e^{-2kL\bar{c}}$$

Since this expression reduces to the equation (5) above, it is seen that the effects of absorption by substances other than ozone cancel in the system of the present invention here as in the device of the prior patent application.

5   As in the above-identified patent application Serial No. 051,651, pressure and temperature transducers are employed. A pressure transducer 80 which may be a commercially available hybrid I.C. laser-trimmed strain gauge having internal temperature compensation and stability of the order of 1% of full scale output is located immediately adjacent the exit outlet of the absorption cell 30 which connects to the outlet line 36. Its voltage output is, of course, fed to the microcomputer of element 72 as in the 10 apparatus of the parent application.

     Similarly, a temperature transducer 82 produces a signal which is fed into the microcomputer of element 72. The temperature transducer is located at approximately the midpoint of the absorption cells and it may be a commercially available device laser-trimmed to produce 298.2 micro-amps output at 298.2° K (25°C). Computations are carried out in a manner similar to that of the parent application,
15 Serial No. 051,651, insofar as the interfacing of the pressure transducer and temperature transducer are concerned.

     The operation of the microcomputer 72 is in fact entirely similar to that of the comparable element in the parent application, Serial No. 051,651 except for the signals which are provided to solenoids 18 and 22. Obviously, the switching of these solenoids to alternate the flow of ambient and ambient-
20 minus-ozone in the manner described above is easily accomplished but follows a somewhat different sequence from the switching of the solenoids or solenoid valves of the parent application.

CLAIMS

     1. An absorption cell gas monitor for monitoring the concentration of a specific gas or vapour in an ambient atmosphere, comprising means for continuously drawing a sample of the ambient atmosphere
25 into an inlet port, a chamber connected to the inlet port and containing material which removes the specific gas or vapour from the ambient sample passing through the chamber, a source of radiation of a predetermined wavelength which is absorbed by the specific gas or vapour, first and second absorption cells each of which is disposed so that radiation from the source passes through it, first means for connecting the outlet from the chamber to the first and second cells alternately to cause periodic flows
30 of the ambient sample from which the specific gas or vapour has been removed through the first and second cells, second means for periodically connecting the inlet port to the second and then the first cell to cause an intermittent flow of the ambient sample through each cell which is out-of-phase with the periodic flow through the cell of the ambient sample from which the specific gas or vapour has been removed, and means for detecting and comparing the absorption of radiation from the source by the
35 contents of the first and second cells in a predetermined sequence.

     2. A monitor according to claim 1, in which the first means for connecting the outlet of the chamber to the first and second cells alternately and the second means for periodically connecting the inlet port to the second and then the first cell comprise a pair of three-way solenoid valves having two inlets and one outlet, and computer means for providing signals which actuate the solenoid valves in a
40 sequence related to the predetermined sequence.

     3. A monitor according to claim 1 or claim 2, in which the specific gas to be monitored is ozone, the material in the chamber comprising metallic oxides for removing ozone from the ambient sample which passes through the chamber, and the means for continuously drawing ambient sample into the inlet port is a continuously operating pump connected to the absorption cells downstream thereof.

45   4. An absorption cell gas monitor for monitoring the concentration of ozone in an ambient atmosphere, comprising means for continuously drawing a sample of the ambient atmosphere into an inlet port, a chamber having an inlet connected to the inlet port and containing material for removing ozone from the ambient sample which passes through the chamber, a source of radiation having a wavelength of substantially 254 nanometers, first and second absorption cells each disposed so that
50 radiation from the source passes through it, first and second three-way solenoid valves each having an inlet connected to the inlet port and another inlet connected to the outlet of the ozone removing chamber, the outlets of the first and second valves being connected to the first and second cells respectively, a microcomputer electrically connected to the first and second valves for controlling their operation in accordance with a predetermined program periodically to cause flow of the ambient sample
55 from which ozone has been removed to the first cell and flow of the ambient sample from the inlet port to the second cell followed by flow of the ambient sample from which ozone has been removed to the second cell and flow of the ambient sample from the inlet port to the first cell, and detection means for detecting the absorption of radiation from the source by the contents of the first and second cells, the detection means being connected to and providing inputs to the microcomputer for storage and
60 computation thereof in a predetermined sequence to provide output data on the concentration of ozone in the ambient sample.